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THERMAL APPLICATIONS FOR ADVANCED METALLIC MATERIALS (PREPRINT)

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14. ABSTRACT
Various applications for advanced metallic materials in the area of thermal management of potential interest to the United States Air Force are discussed. Particular emphasis is given to the following technologies; passive thermal systems utilizing high thermal conductivity metallic composites; lightweight metallic phase-change materials for managing thermal transients; high-efficiency thermoelectric materials for energy harvesting applications. In this paper, a brief background of the current SOA in each technology is presented, along with potential new areas for growing new research directions. Strategies for short-, medium-, and long-term materials and systems development are proposed.

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THERMAL APPLICATIONS FOR ADVANCED METALLIC MATERIALS

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ABSTRACT

Various applications for advanced metallic materials in the area of thermal management of potential interest to the United States Air Force are discussed. Particular emphasis is given to the following technologies; passive thermal systems utilizing high thermal conductivity metallic composites; lightweight metallic phase-change materials for managing thermal transients; high-efficiency thermoelectric materials for energy harvesting applications. In this paper, a brief background of the current SOA in each technology is presented, along with potential new areas for growing new research directions. Strategies for short-, medium-, and long-term materials and systems development are proposed.

KEYWORDS: Thermal Management/Control; Thermal Protection/Thermal Protection Materials; Thermal Analysis.

1. INTRODUCTION

Metallic materials have a number of attractive mechanical, physical and engineering properties which make them ideal candidates for thermal applications of increasing interest to the United States Air Force. As future missions become more demanding, increased thermal performance of aircraft systems may become an increasingly important factor in component design and materials selection/development. In addition, fuel conservation via improved fuel efficiency is becoming a top priority for many large organizations, both inside and outside of the DoD, with decreased logistical footprints and reduced operational costs as prime motivators. Thermal applications for metallic materials include both thermal *management* (i.e. the conduction, convection and radiation of unwanted thermal energy within a structure to prevent failure) and thermal *protection* (i.e. heat shielding to prevent the underlying structure from overheating, especially for re-entry vehicles). Although the two are closely inter-related, this paper will focus mainly on the first topic, with reference to thermal protection where appropriate.

2. MATERIALS SYSTEMS OF INTEREST

2.1 Ultra-High Thermal Conductivity Metallic Composites Oxygen-Free High Conductivity (OFHC) copper is often considered as a baseline material for comparing thermal conductivities of other metallic and composite materials. Handbook data shows that K_{th} for OFHC copper is

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around 400 W/m·K at room temperature, decreasing to ~ 360 W/m·K at 800K. Materials with thermal conductivities exceeding these values can therefore be considered as *Ultra-High Thermal Conductivity* materials [1]. One common approach for obtaining increased mechanical and physical properties for advanced materials is by forming a composite microstructure of two (or more) different materials, thereby obtaining an attractive combination of the mechanical and physical properties of the constituent phases. The upper limit to thermal conductivity (K_{th}) of a two-phase composite material (matrix plus particulate reinforcement) can be reasonably estimated as a function of reinforcement volume fraction (*f*) and temperature (*T*) via Eqn. (1) due to Hasselman and Johnson [2].

$$K_{th}(T) = K_m(T)\left[\frac{(2f+1)K_d(T)+2(1-f)K_m(T)}{(1-f)K_d(T)+(2+f)K_m(T)}\right] \quad (1)$$

Here, subscript *m* refers to the matrix and subscript *d* refers to the reinforcement. In reality, however, interfacial resistance between the matrix and reinforcement phases tends to decrease the effective thermal conductivity of the material well below this upper limit. This interfacial thermal barrier resistance is a function of reinforcement size, reinforcement spatial distribution and the chemical and mechanical state of the interface [3]. A reasonable approach for producing a metallic composite with a thermal conductivity higher than OFHC copper would be to start with a copper matrix and then introduce a high thermal conductivity reinforcing particle, such as diamond (K_d > 1000 W/m·K). For example, a block of Cu-40% diamond composite material was produced by direct powder forging[a]. The thermal conductivity of this material was measured (using a laser flash diffusivity technique) to be 588 W/m·K at room temperature, an improvement of 47% over the OFHC copper baseline. This figure also agrees well with the prediction of 585 W/mK from Eqn. (1), using values of K_m = 400 W/m·K and K_d = 1000 W/m·K, suggesting that interfacial thermal barrier resistance in this particular material was negligible. Other experimental data available in the open literature [3] suggests even higher thermal conductivities (up to 740 W/m·K) may be obtainable with higher volume fractions of diamond (up to 70%) and large particles (90–110 μm). These authors also reported TEM results suggesting that the copper-diamond interface was of good quality.

In general, increasing the volume fraction of diamond reinforcement will decrease the coefficient of thermal expansion (α) of the composite material, since diamond has an α of around 0.5×10^{-6}/K, compared with Cu at around 17×10^{-6}/K [4]. Eqn. (2) obtained by Kerner [5] is often used to predict α, based on the volume fraction of reinforcement (*f*), and the thermal expansion coefficients (α), bulk moduli (*B*) and shear moduli (*G*) of the constituent phases.

$$\alpha = \alpha_m + f(\alpha_d - \alpha_m)\cdot\left[\frac{B_m(3B_d+4G_m)^2+(B_d-B_m)(16G_m^2+12G_mB_d)}{(4G_m+3B_d)[4fG_m(B_d-B_m)+3B_mB_d+4G_mB_m]}\right] \quad (2)$$

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[a] Ceracon, Inc., Fair Oaks, CA.

For example, a Cu-40% diamond composite is predicted to have $\alpha = 7.9 \times 10^{-6}$/K for the following constitutive properties; $\alpha_m = 17 \times 10^{-6}$/K; $\alpha_d = 0.5 \times 10^{-6}$/K; $B_m = 121$ GPa; $B_d = 580$ GPa; $G_m = 69$ GPa; $G_d = 360$ GPa [3, 4]. A useful reduction in α compared with the unreinforced metal has important ramifications for microelectronics packaging and heat-spreader applications where the coefficient of thermal expansion of the package must be matched with that of the semiconductor substrate to avoid thermal stresses and thermo-mechanical fatigue [6]. A suitable figure of merit for design purposes therefore might be the ratio K_{th}/α. Table 1 shows the thermal properties for a number of metallic composite materials currently being used and under development.

Table 1: Metallic composite materials for thermal management applications.

Material system	vol. frac (f)	K_{th} (W/m·K)	α ($\times 10^{-6}$/K)	K_{th}/α (W/μm)	Notes
Al-SiC	0.6	170 – 200	6.5 – 9.0	22 – 26	current SOA, tradename "AlSiC" [7]
Cu-SiC	0.3	300	11	27	under development [8]
Cu-SiC	0.6	260	9.5	27	under development [8]
Cu-d*	0.4	588	11	53	under development [8, 9]
Al-d*	–	550-600	7-7.5	80	under development [6]

* diamond particles.

It should also be noted that these thermal properties are often isotropic or near-isotropic, depending on the chosen processing route, which can be advantageous in that it makes the component designer's task easier. Typical applications for these types of materials include heat sinks and heat spreaders for microelectronics, and enclosures for microelectronic, optoelectronic and microwave packaging. In the latter case, hermeticity is an important attribute (i.e. these materials are typically fully dense with no porosity) as is electrical conductivity (for EMI shielding). For some of the more demanding military applications, mechanical properties can also be a design factor, especially stiffness, fatigue resistance, strength and wear behavior.

2.2 Metallic Phase-Change Materials A phase change material (PCM) is one in which either the latent heat of fusion (solid $\Leftrightarrow$ liquid) or the latent heat of evaporation (liquid $\Leftrightarrow$ vapor) is utilized as a source or a sink for thermal energy. In a reversible phase transformation at constant temperature and pressure, the heat (enthalpy) which can be stored (or released) by the PCM is simply the product of the entropy change and the absolute transformation temperature, i.e. $\Delta H = T\Delta S$. Many metallic elements have high latent heats of fusion, due to their reasonably-high entropies of fusion (around 10 kJ/kg for hcp and fcc metals [10]) and high absolute melting temperatures, which make them attractive candidates as PCMs for thermal energy storage (TES) systems. Even though much higher enthalpies are generally associated with the latent heat of evaporation (due to the much larger entropy change associated with this phase transformation) the practicalities of dealing with large volume changes may preclude their use for TES due to containment issues, however, the evaporation/condensation phase transformation can still be

very effectively employed in heat pipes. Although this particular application is beyond the scope of the present paper, the reader is referred to the excellent texts by Faghri [11], and Fraas [12].

2.2.1 The Solid-to-Liquid Phase Transformation Although the number of pure metallic elements that can be considered for PCM duty is somewhat limited, a very large number of candidate metallic PCMs can be explored via alloying, guided by thermodynamic principles. Eutectic alloys and near-eutectic alloys are particularly attractive [13, 14], as they can have high entropies of mixing, and transform approximately isothermally, which has advantages in TES system design [15]. A further advantage [16] of metals is that they can have one or two orders of magnitude higher thermal conductivities compared to equivalent molten salt systems (LiF, LiF-CaF_2, NaF etc.). This can lead to significant improvements in efficiency, and lead to simpler system designs due to reduced thermal gradients. Predicting the latent heat of fusion of even a simple binary eutectic is not trivial, and the work of Birchenall and Riechman can be very useful as a guide for exploring candidate binary systems, and can be extended to ternary and higher alloys if desired. For the case of a binary eutectic (*A*–*B*) with limited solid solubility of the terminal phases, the following expression is provided [14]:

$$\Delta S = -R \left\{ \begin{array}{l} (1-x_e)ln(1-x_e) + x_e\ ln\ x_e - \\ \left(\dfrac{x_\beta - x_e}{x_\beta - x_\alpha}\right)[(1-x_\alpha)ln(1-x_\alpha) + x_\alpha\ ln\ x_\alpha] - \\ \left(\dfrac{x_e - x_\alpha}{x_\beta - x_\alpha}\right)[(1-x_\beta)ln(1-x_\beta) + x_\beta\ ln\ x_\beta] \end{array} \right\} + (1-x_e)\frac{L_A}{T_A} + x_e\ \frac{L_B}{T_B} \qquad (3)$$

Here, x_e is the eutectic composition, x_α is the limit of solid solubility for *B* in *(A)*, $(1-x_\beta)$ is the limit of solid solubility for and *A* in *(B)*, and L_A, L_B, T_A and T_B refer to the latent heats of fusion and absolute melting temperatures of the pure elements, *A* and *B*, respectively. It can be seen that elements with the highest entropies of fusion will give the largest contribution to the overall *ΔS*.

Table 2: Binary and ternary eutectic systems which show particular promise as metallic PCMs.

Eutectic	ΔH_f (kJ/kg)	T_e (K)	$\Delta H_f / T_e$ (kJ/kg·K)	[Reference]
Al-Si	515	851	0.605	[14]
Al-Ge	368	712	0.532	(evaluated (Eqn. 3))
Mg-Si	774	1219	0.635	[14]
Mg-Ge	496	969	0.511	(evaluated (Eqn. 3))
Al-Si-Mg	545	833	0.654	[14]
Si	1800	1687	1.067	[17]
Be-Si	1350	1363	0.990	[17]
Ca-Si	1100	1296	0.849	[17]

The predictive capabilities of this kind of analysis are still limited by the availability of reliable thermodynamic data. However, many alloys have been investigated for their potential as metallic PCMs, for a variety of different applications and temperature ranges [13-18], however, a smaller number of binary and ternary alloys, based on aluminum, magnesium, silicon and germanium show particular promise, Table 2.

For example, in the prototype binary eutectic system Al-Si [19], there is limited solid solubility of Si in (Al) and close to zero solubility for Al in (Si). Even though the eutectic alloy only contains 12.2 at.% Si, the high latent heat of fusion of this semi-metal (1790 kJ/kg) translates into an overall ΔH_f of ~ 515 kJ/kg [14]. Therefore, other eutectic alloys which contain greater amounts of the Si phase should also be investigated (e.g. Mg-MgSi$_2$, Ca-CaSi$_2$ and Sr-SrSi$_2$ eutectics). In addition to the binary eutectics, ternary alloying additions can be used to decrease the eutectic temperature and thereby increase the ratio $\Delta H_f / T_e$, which is often used as a figure-of-merit for PCMs. One example is the ternary system Al-Si-Mg shown in Figure 2, where a ternary eutectic (T_e = 833 K) exists at the composition 82.3 Al-12.6 Si-5.1 Mg (Wt%) [20]. By adding Mg to the binary Al-Si alloy, it is possible to simultaneously increase ΔH_f and decrease T_e, thereby increasing the ratio of $\Delta H_f / T_e$ from 0.605 to 0.654.

2.2.2 Design Considerations Although the high latent heat of fusion and high thermal conductivity may be among the primary factors for selecting a metallic alloys as PCMs, additional considerations come into focus when designing a practical TES. Containment of the PCM is of primary importance [15, 18], especially when there is a large volume change upon solidification which must be accommodated at elevated temperatures. The need for chemical compatibility of the container with molten metallic constituents may suggest ceramics, oxides, and/or high-temperature refractory metals as suitable containers, which can present significant challenges with thermal expansion, thermal shock and thermo-mechanical fatigue. This is especially acute when extended service life is required (for example, an on-orbit solar power generating system [16] where maintenance may be expensive or impossible during the lifetime of the spacecraft.) Thermal cycling may also cause performance degradations in terms of nucleation of the solid on the walls of the containment vessel over repeated cycling. This will increase the response time of the unit by increasing the superheating/undercooling characteristics of the PCM and also decrease the available ΔH_f for energy storage. Other considerations include density (for other than ground-based systems), environmental factors (e.g. Be-Si makes a very effective PCM, see Table 2) and raw material and processing costs. A number of suitable applications exist for these materials, both in thermal management and in thermal protection, wherever potentially-damaging high transient heat fluxes exist. One concept currently under investigation is the feasibility of using a high-temperature metallic PCM as part of a thermal protection system for re-entry vehicles. The PCM could absorb the heat fluxes generated during atmospheric heating, protecting other more critical parts of the reentry vehicle. Once on the ground, the PCM would slowly cool and reject the heat back to the structure in a safe manner.

2.3 High-Temperature Bulk Thermoelectric Materials The thermoelectric effect has been well documented in metals and semiconductors for over 150 years, starting with the observations of thermoelectric cooling first made by Peltier in 1834. For example, the thermoelectric effect is

the basis of all thermocouples used routinely for temperature measurement, and bismuth telluride thermo-coolers are now available for beverage chillers in high-end automobile gloveboxes. Figure 1 shows a schematic (after [21]) of a typical thermoelectric couple, configured (a) for active refrigeration, and (b) for power generation. In this example, the couple is made from an *n*-type semiconductor and a *p*-type semiconductor, arranged *electrically in series*, and *thermally in parallel*.
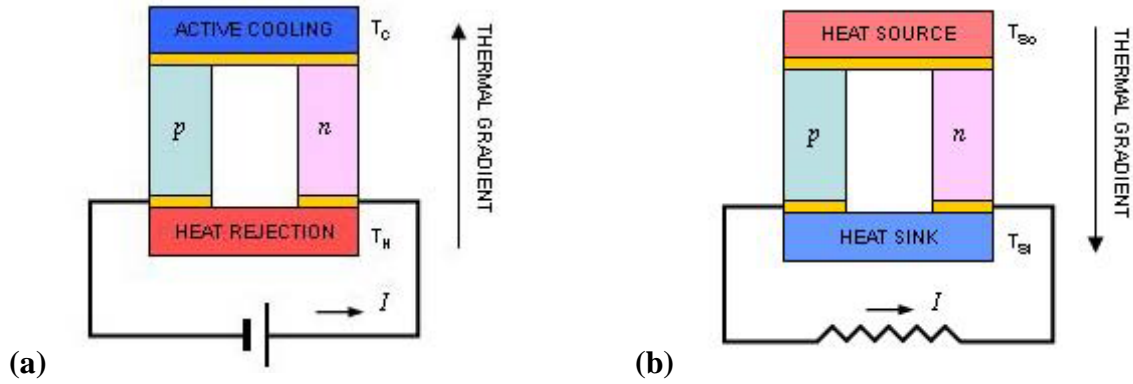

(a)   **(b)**

Fig. 1. Schematic showing a typical thermoelectric couple comprising *n*-type and *p*-type semiconductors joined by ohmic contacts to the external circuit; (a) for active refrigeration where $T_H - T_C \geq 0$, and (b) for power generation where $T_{So} - T_{Si} \geq 0$. (after [21]).

The basic equation which determines the figure-of-merit (*ZT*) for a thermoelectric material at a prescribed temperature *T* is given by Eqn. (4),

$$ZT = \frac{S^2 \sigma T}{K} \qquad (4)$$

Here, *S* is the Seebeck coefficient which is a material parameter which must be measured, σ is the electrical conductivity (in $\Omega^{-1} \cdot m^{-1}$) and *K* is the thermal conductivity (in W/m·K). Likewise, the effective *ZT* of the *p–n* couple depicted in Fig. (3) is given by Eqn. (5).

$$ZT_{p-n} = \frac{(S_p - S_n)^2 T}{\sqrt{K_p/\sigma_p} + \sqrt{K_n/\sigma_n}} \qquad (5)$$

The overall thermodynamic efficiency of the thermoelectric device will be determined [22] by the product of the effective *ZT* and the Carnot efficiency, thus:

$$\eta = \left(\frac{T_H - T_C}{T_H}\right) \cdot \frac{\sqrt{1 + \overline{ZT}} - 1}{\sqrt{1 + \overline{ZT}} + (T_C/T_H)} \qquad (6)$$

Thermodynamic efficiencies for the highest *ZT* thermoelectric materials can reach up to 20%. Although this is poor in an absolute sense, even slight improvements in *ZT* beyond this value can be enabling for many applications. Many of the current efforts [23] to maximize *ZT* are concerned with maximizing σ whilst simultaneously minimizing *K*. However, in most materials the two are positively correlated making the task a challenging one. Nevertheless, a number of approaches have been identified, including the development of complex inorganics such as Pb-Ag-Sb-Te (LAST*m*) [24], layered metal oxides (NaCo$_2$O$_4$ etc.) [25], Skutterudites (CeFeCoSb, etc.) [26] and the Half-Heusler alloys e.g. *M*NiSn, where *M* = Ti, Zr, Hf [27]. However, one can also usefully improve efficiency by increasing the temperature of operation (see Eqn. (6)), which means environmental stability becomes an important issue for many of these systems. Some materials can behave adversely at elevated temperatures, including rapid sublimation [28, 29], thereby reducing their effectiveness and limiting their performance envelope.
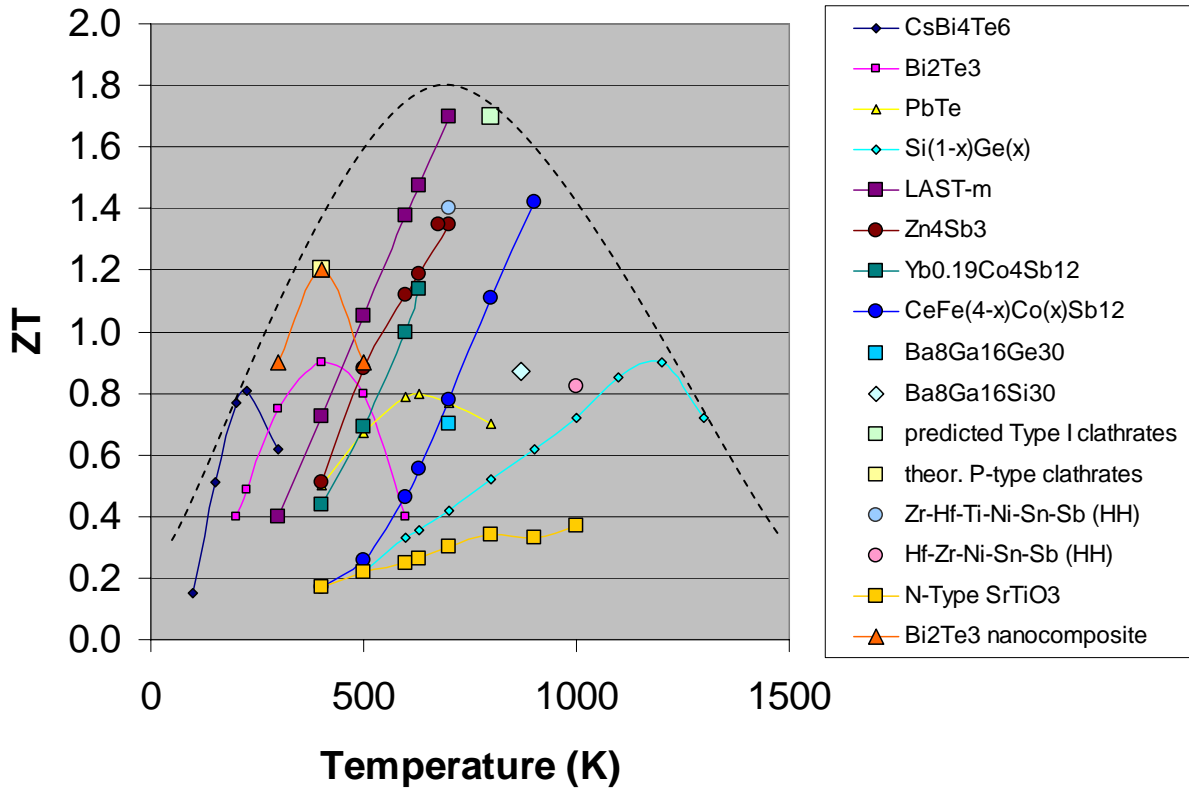

Fig. 2. Plot showing thermoelectric figure-of-merit, *ZT*, vs. absolute temperature, *T*, for various bulk materials currently under development. Note that in spite of recent developments in other systems, for the highest temperatures (up to 1200 K), Si$_x$Ge$_{(1-x)}$ semiconducting alloys are still highly competitive.

Additional factors for consideration are mass density (for example, some thermoelectrics containing the heavy elements lead and silver have shown exceptional *ZT*), toxicity and cost. A more in-depth discussion of the most recent developments in both bulk and reduced-dimension thermoelectric materials can be found in the recent set of articles published in MRS Bulletin [21,

23, 29-32]. Figure 2 is a compilation of experimentally-measured *ZT* values, obtained from the open literature[b], plotted *vs.* absolute temperature.

2.3.1 Applications As mentioned above, the two main applications for bulk thermoelectrics are in (a) active cooling of hot structures (including electronics), and (b) electrical power generation. As power requirements in aircraft and spacecraft systems increase, there is a lot of waste heat which must be accommodated in the structure. Thermal management of this waste heat using thermoelectric refrigeration is a tantalizing prospect. Thermoelectric coolers have no moving parts, are silent, and although they typically have high mass densities, they may provide substantial weight savings on a system level when compared to traditional (thermodynamic phase change) cooling systems using pumps, ducts, lines, tanks and working fluid(s). Further advantages include the ability to locally cool hot spots on components or structures on demand, with a reasonably-fast response time. One application could be the use of thermoelectric coolers for avionics cooling rather than using a pumped-fluid cooling system.

In concert with efforts to provide on-board cooling, thermoelectric materials are also being researched as electrical power generating materials. The Air Force Office of Scientific Research has recently awarded a multi-university five-year program on multifunctional materials development for energy *harvesting* [33], that is, turning waste heat, light and mechanical (vibration) energy into useful electrical energy on board air vehicles and space platforms. Bulk thermoelectric materials are expected to play a major role in this initiative, with a focus on the science behind improving efficiencies in these systems. Aerodynamic heating is one thermal source which could be usefully employed to provide distributed power to aircraft systems, for built-in diagnostic sensing for example. In this case, the issue of inherently low overall energy conversion efficiency can be outweighed by the unique requirements of the application, as is the case for radioisotope thermoelectric generators (RTGs) used in NASA's deep space probes for over 30 years [29, 34].

4. FUTURE RESEARCH DIRECTIONS

4.1 Ultra-High Thermal Conductivity Metallic Composites The current SOA in high thermal conductivity metallic composites is based on the Al-SiC system, which provides adequate balance of properties for thermal loads currently found in microelectronics and microwave devices. However, as thermal loads continue to increase with reductions in die size and/or increases in processor speed, there will always be a need for improved thermal conductivity and/or reduced thermal expansion in these materials. The next logical step for these materials will be the incorporation of higher thermal conductivity reinforcements such as diamond into higher thermal conductivity matrices such as copper and copper alloys. In the short term, work should center on controlling the structure and chemistry of the matrix–reinforcement interface, to minimize thermal barrier resistance and improve mechanical properties (which can translate into increased processability, for example). Additional research into the enhancement of thermal properties via microstructural control of the spatial distribution of the reinforcement is also

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[b] Figure courtesy of Capt. W. Sanders, AFRL/EAORD.

worthwhile, as initial modeling results have shown there is a measurable effect here. The incorporation of high thermal conductivity particles into high temperature matrix materials should also be investigated for those demanding applications where high thermal conductivity is required at temperatures other than ambient, and issues such as creep and thermo-mechanical fatigue become design drivers.

4.2 Metallic Phase-Change Materials Potential applications for phase change materials as energy storage media are numerous, both for ground-based systems and airborne platforms. In the short term, issues such as containment and environmental compatibility should be addressed for the most promising metallic systems based on eutectic and near-eutectic alloys, especially the higher-temperature alloys based on Ca, Be and Si. Feasibility studies for incorporating these kinds of PCM system into re-entry vehicle TPS concepts could be highly informative. For medium to long-term efforts, alloy development for thermal properties is a potential growth area. Especially in the case of high-temperature *structural* alloys, thermal properties are not typically designed for, even though they may play a role in material or component performance. The concept of designing chemistries and microstructures to afford enhanced thermal properties is an intriguing one. Modern, thermodynamics-based computational materials design could be usefully employed in this regard; for example in exploring ternary and higher phase equilibria for deep eutectics beyond what has been done before [14] or using combinatorial approaches to multi-phase alloy design.

4.3 High-Temperature Bulk Thermoelectric Materials In the short term, one of the most pressing needs which is not being addressed currently is increased processability. The current SOA in medium–high temperature (600 – 800 K) thermoelectric materials are based on Pb-Ag-Sb-Te [24], and CeFeCoSb [26] chemistries. These materials are limited in temperature primarily by material breakdown and environmental effects. The ability to process these materials in such a way that they would be immune to these issues would be enabling for demonstrating a useful prototype device, since much of the investigative work on these systems to date has been done on materials that were not processed using optimal conditions. In the medium and long-terms, research into higher-temperature and more durable thermoelectric materials through manipulation of materials chemistry and microstructure on the nanoscale has great potential for success. By directly and independently manipulating the chemistry and nanostructure of these materials, new methods for maximizing σ whilst simultaneously minimizing K could be established, with obvious benefit in terms of a breakthrough in thermal efficiency.

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